

Characterization of CO₂ Hydrogenation Catalysts in Reverse Water Gas Shift

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Background

With increasing quantities of greenhouse gases, efforts are growing to reduce the dependencies on energies derived from fossil fuels by using alternative, renewable forms of energy. Power-to-gas technology allows for more effective use of renewable energies by driving the hydrogenation of CO₂. CO₂ hydrogenation facilitates the reuse of carbon by converting it into synthetic gases and fuels. This is done by selectively producing CO by reverse water gas shift (RWGS) catalysis, which is then hydrogenated into hydrocarbon chains by Fischer-Tropsch synthesis (FTS) or methanation processes. The hydrogen can be derived from various methods like steam reforming of light alcohols or electrolysis. The following reactions were in study:

- RWGS: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
- Methanation: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$
- FTS: $\text{CO} + 2\text{H}_2 \rightarrow -[\text{CH}_2]_n + \text{H}_2\text{O}$

Skills/Objectives

- To make and characterize various sodium-doped cobalt zirconia catalysts
- Characterization was done through TPR analysis, infrared spectroscopy, and mass spectrometry.
- Analysis of formate, methane and CO detections at various temperatures and sodium concentrations

Future Studies

Further catalyst testing will be conducted at the University of Kentucky for applied energy research. Further optimization of sodium loadings can be researched to provide more selectivity.

Methods

Alfa Aesar (Stock No. 43815) monoclinic ZrO₂ 1/8" pellets were crushed and sieved to 63 – 106 microns. An aqueous solution of Co(II)(NO₃)₂·6H₂O was introduced to the sieved zirconia base by incipient wetness impregnation, followed by calcination at 350°C. This batch was divided into other batches for loadings of Na: 0.5%, 1%, 1.8%, 2.5%, and 5% by the same technique. For the 5% sodium batch, two impregnations were conducted to avoid reaching the solubility limit of NaNO₃ in water. Further calcinations were done followed by a hydrogen activation to prepare the catalyst for characterization.

Results

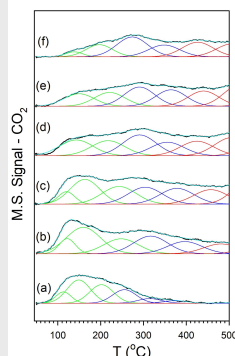


Figure 1: CO₂ TPD-MS profiles for 5% Co/m-ZrO₂ catalyst with (a) 0%Na, (b) 0.5%Na, (c) 1%Na, (d) 1.8%Na, (e) 2.5%Na, (f) 5%Na dopings including Gaussian fittings

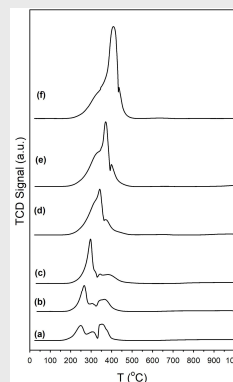


Figure 2: H₂ TPR TCD profile for 5% Co/m-ZrO₂ catalyst with (a) 0%Na, (b) 0.5%Na, (c) 1%Na, (d) 1.8%Na, (e) 2.5%Na, (f) 5%Na dopings

Catalyst	%		
	T < 250°C	250°C < T < 400°C	% T > 400°C
5%Co/m-ZrO ₂	70	29	1
0.5%Na-5%Co/m-ZrO ₂	57	35	8
1%Na-5%Co/m-ZrO ₂	49	35	16
1.8%Na-5%Co/m-ZrO ₂	35	39	26
2.5%Na-5%Co/m-ZrO ₂	32	43	25
5%Na-5%Co/m-ZrO ₂	20	47	33

Figure 3: Results of fitting CO₂ TPD profiles with Gaussian peaks.

Catalyst	Carbonate bands	Formate bands	T (°C) formate detected	T (°C) formate maximum	T (°C) CH ₄ (g) detected	T (°C) CO (g) detected
			15°C (from OCO)	300°C (from OCO)	115°C	375°C
5%Co/m-ZrO ₂	1692, 1556, 1473, 1420, 1344, 1276, 1223, 1049	1549, 1357, 1304	200°C (from OCO)	300°C (from OCO)	200°C	375°C
w/ 0.5%Na	(lb) 1677, 1632, 1514, 1226, 1049	1554, 1336, (lb) 1505, 1405, 1248	250 - 275°C (from CH)	325°C (from CH)	250 - 275°C	250°C
w/ 1.8%Na	(lb) 1684, 1657, 1530, 1079, 1006	2800, 1620, 1329, 1218, 1079, 1006	250°C (from CH)	300°C (from CH)	300°C	225°C
w/ 2.5%Na	(lb) 1677, 1640, 1530, 1344, 1205, 1064, 1004	2800, 1612, 1335	250°C (from CH)	300°C (from CH)	275°C (250°C very slight)	225°C
w/ 5%Na	(lb) 1679, 1620, 1520 - 1460, 1355, 1064, 1007, 951	2800, 1606, 1349	250°C (from CH)	300°C (from CH)	275°C (250°C very slight)	225°C

Figure 4: Band assignments and key features from DRIFTS of 4%CO₂ + 60%H₂ (balance He).

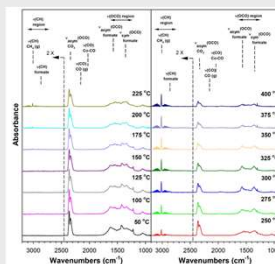


Figure 5: DRIFTS of 4%CO₂ + 60%H₂ (balance He) over 5%Co/m-ZrO₂.

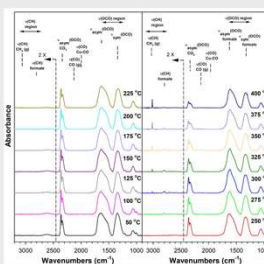


Figure 6: DRIFTS of 4%CO₂ + 60%H₂ (balance He) over 2.5%Na-5%Co/m-ZrO₂.

Conclusions/Discussion

- Figure 1 shows that the basicity of the catalyst increases with higher Na concentrations. This allows for stronger CO₂ bonding interactions but also inhibits H₂ dissociation during activation of the catalyst.
- Gaussian fittings were conducted to find percentages of different maxima at three temperature ranges as shown in Figure 3
- Figure 2 shows catalyst activation temperatures for different loadings of Na. These peaks get larger with higher loadings of Na due to more carbonate forming on the surface. This is corroborated by the mass spectrometry data showing that more CO_x species are removed during the activation.
- Figure 4 shows that methane is detected at higher temperatures with increasing sodium content, as well as lower temperatures for CO. This shows that there is selectivity in production of CO, making it more ideal for production of hydrocarbons larger than methane.
- Figure 5 shows the characteristics of the unpromoted catalyst. The spectra shows that methane is observed at relatively low temperatures (175°C) and CO at high temperatures (375°C).
- Figure 6 shows the characteristics of the 2.5% promoted catalyst. The spectra shows that methane is produced at high temperatures (375°C) and that CO is produced at low temperatures (225°C)

From the spectra and Figure 4, 2.5% Na was found to be the most optimal loading of sodium from the batches made in terms of CO and CH₄ selectivity. At this loading, the temperature at which methane formed was at a maximum and the temperature for CO production was at a minimum. This would facilitate more optimal hydrocarbon synthesis due to higher CO conversions.

References

- Michela Martinelli, Jonathan D. Castro, Nour Alhraki, Maria E. Matamoros, A. Jeremy Kropf, Donald C. Cronauer, Gary Jacobs, Effect of sodium loading on Pt/ZrO₂ during ethanol steam reforming, Applied Catalysis A: General, Volume 610, 2021, 117947, ISSN 0926-860X, <https://doi.org/10.1016/j.apcata.2020.117947>.
- Lizandra M.N.C. Alves, Mayra P. Almeida, Martin Ayala, Caleb D. Watson, Gary Jacobs, Raimundo C. Rabelo-Neto, Fabio B. Noronha, Lisiane V. Mattos, CO₂ methanation over metal catalysts supported on ZrO₂: Effect of the nature of the metallic phase on catalytic performance, Chemical Engineering Science, Volume 239, 2021, 116604, ISSN 0009-2509, <https://doi.org/10.1016/j.ces.2021.116604>.

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